Search for variation of the fundamental constants in atomic, molecular and nuclear spectra

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The search for variation of the fundamental constants such as the fine structure constant α ($\alpha = e^2/\hbar c$) and the ratios of fundamental masses (e.g., electron to proton mass ratio $\mu = m_e/m_p$) is reviewed. Strong emphasis is given to establishing the relationships between the change in the measured frequencies of atomic, molecular or nuclear transitions and the corresponding change of the fundamental constants. Transitions in which the sensitivity of the frequency change to the variation of the fine structure constant is strongly enhanced are discussed and most recent experimental results are presented. Most attention is given to the use of atomic, molecular and nuclear transitions in the study of quasar absorption spectra and in atomic clock experiments.

I. INTRODUCTION

Search for variation of the fundamental constants is now a very popular area of research. It is motivated by theories unifying gravity with other interactions as well as many cosmological models which suggest a possibility for fundamental constants to very in space and time. Hints that some fundamental constants might had slightly different values in distant past have been found in Big Bang nucleosynthesis, quasar absorption spectra and Oklo natural nuclear reactor (see, e.g reviews [1, 2]). However, most of publications report only constrains on possible variation of the fundamental constant. For example, strong limits on present-day time variation of the fine structure constant and lepton to hadron mass ratio come from atomic clock experiments (see, e.g. [2, 3]).

Good progress in the search for the manifestation of the variation of the fine structure constant in quasar absorption spectra was achieved with a very sensitive many-multiplet (MM) method which was suggested in Ref. [4]. The analysis of the data from 143 absorption systems revealed anomalies in atomic spectra which can be best explained by assuming a slightly smaller value of the fine structure constant about 10 billion years ago [5].

The MM method relies on atomic calculations to relate the variation of the frequencies of atomic transitions to the variation of the fine structure constant. Similar calculations for the atomic transitions which are used or planed to be used as atomic optical frequency standards also allowed to extend this fast developing area of research to the study of the present-date time variation of the fine structure and other constants.

It only makes sense to consider variation of dimensionless constants (see, e.g. [1]). Therefore, most of the research is focused on the study of either variation of the fine structure constant α ($\alpha = e^2/\hbar c$) or electron to proton mass ratio $\mu = m_e/m_p$ or some other fundamental mass ratio like, e.g.
$m_{e,q}/\Lambda_{QCD}$ where m_q is the quark mass and Λ_{QCD} is the quantum chromodynamics mass scale defined as a position of Landau pole in the logarithm for the running

strong coupling constants. Models of the grand unification suggest that if fundamental constants vary than fundamental mass ratio varies faster that the fine structure constant and therefore it might be easier to detect it. Transitions sensitive to the variation of the mass ratio can be found in atomic microwave, molecular and nuclear spectra. Corresponding studies use quasar absorption spectra and laboratory measurements [2].

Further advance in sensitivity can be achieved if strong enhancement is found. The relative rate of frequency change ($\dot{\omega}/\omega$) due to change of the fundamental constants is usually inversely proportional to the energy interval between the two states $\hbar\omega$. Therefore the relative enhancement is likely to be found for the pairs of almost degenerate long-living states of significantly different nature. Different nature of states is important to make sure that they don't move with the same rate. Also, long lifetime is needed for high accuracy of the frequency measurements. Pairs of states which satisfy all these conditions can be found in atomic, molecular and nuclear spectra.

In present paper we review the search for variation of the fundamental constants focusing of the connections between measured values and the change of the fundamental constants, enhancement mechanisms and most recent experimental results.

II. OPTICAL ATOMIC SPECTRA

The use of optical atomic transitions in the search for variation of the fine structure constant α is based on the fact that the frequencies of these transitions depend differently on α and one can compare the frequencies of different transitions over long period of time. If α is changing the ratio of the frequencies would change too.

In atomic units $\alpha = 1/c$ where c is speed of light. Therefore, $\alpha = 0$ correspond to a non-relativistic limit. Leading relativistic corrections are proportional to $(Z\alpha)^2$ where Z is nuclear charge. Therefore, it is convenient to present the dependence of atomic frequencies on the fine-structure constant α in the vicinity of its physical value

α_0 in the form

$$\omega(x) = \omega_0 + qx, \tag{1}$$

where ω_0 is the present laboratory value of the frequency and $x = (\alpha/\alpha_0)^2 - 1$. The sensitivity coefficient q is to be found from atomic calculations.

Note that

$$q = \left. \frac{d\omega}{dx} \right|_{x=0}. \tag{2}$$

To calculate this derivative numerically we use

$$q \approx \frac{\omega(+\delta) - \omega(-\delta)}{2\delta}. \tag{3}$$

and vary the value of α in the computer code.

The same formula (1) and similar atomic calculations are used for the analysis of quasar absorption spectra and for laboratory experiments involving optical transitions. A review of the methods of atomic calculations and critical compilation of the results for the quasar absorption spectra are presented elsewhere [6]. Below we review the latest results of the analysis and discuss the results of calculations for the laboratory measurements.

A.   Comparison of quasar absorption spectra with laboratory spectra

The analysis of the three independent samples of data containing 143 absorption systems spread over red shift range $0.2 < z < 4.2$ gives [5]

$$\frac{\delta\alpha}{\alpha} = (-0.543 \pm 0.116) \times 10^{-5}. \tag{4}$$

If one assumes the linear dependence of α on time, the fit of the data gives

$$\delta\alpha/\alpha = (6.40 \pm 1.35) \times 10^{-16}/\text{yr}, \tag{5}$$

per year over time interval of about 12 billion years. A very extensive search for possible systematic errors has shown that known systematic effects can not explain the result [7].

Recently our method and calculations [4, 8, 9, 10] were used by two other groups [11, 12, 13]. However, they have not detected any variation of α. The results of [11] were questioned in Refs. [14, 15]. Re-analysis of Ref. [11] data revealed flawed parameter estimation methods. The authors of [14, 15] claim that the same spectral data fitted more accurately give $\frac{\delta\alpha}{\alpha} = (-0.64 \pm 0.36) \times 10^{-5}$ (instead of $\frac{\delta\alpha}{\alpha} = (-0.06 \pm 0.06) \times 10^{-5}$ in Ref.[11]). However, even this revised result may require further revision.

Note that the results of [5] are based on the data from the Keck telescope which is located in the Northern hemisphere (Hawaii). The results of [11, 12, 13, 14, 15] are based on the data from the different telescope (VLT) located in the Southern hemisphere (Chile). Therefore, some difference in the results may appear due to the spatial variation of α.

B.   Optical atomic clocks

Study of the atomic optical frequency standards is huge and fast developing area of research. The accuracy of the measurements of atomic transitions between the ground and a metastable excited state for some atoms are on the level of 10^{-16} with good prospects for further improvements (see, e.g. [3]). This makes it possible to use atomic frequency standards to study present-day time variation of α and other fundamental constants. This is done by comparing frequencies of different atomic transition over long period of times. One has to know how the frequencies depend of α for the interpretation of the results. We have performed relativistic many-body calculations [8, 17, 18, 19, 20, 21, 22] similar to those used in the analysis of the quasar absorption spectra to establish this dependence. The results are summarized in Tables I and II. Calculated energies are included to illustrate the accuracy of the calculations. The q coefficients for optical clock transitions may be substantially larger than those used in cosmic transitions since the clock transitions are often in heavy atoms (Hg II, Yb II, Yb III, etc.) while cosmic spectra contain mostly lines of light atoms ($Z < 33$). The relativistic effects are proportional to $Z^2\alpha^2$.

Combined analysis of the frequency shifts of optical transitions in H [23], Yb$^+$ [24], Hg$^+$ [25] and Sr [26] as measured against Cs primary frequency standard gives the following limit on the rate of time-change of α and $\mu = m_e/m_p$ [26]

$$\delta\alpha/\alpha = (-3.3 \pm 3.0) \times 10^{-16}/\text{yr}, \tag{6}$$
$$\delta\mu/\mu = (1.6 \pm 1.7) \times 10^{-15}/\text{yr}. \tag{7}$$

In a more recent work [27] in which optical frequencies of Al$^+$ and Hg$^+$ were compared over a year the variation of α is limited by

$$\delta\alpha/\alpha = (-1.6 \pm 2.3) \times 10^{-17}/\text{yr}. \tag{8}$$

The results for $\delta\alpha/\alpha$ (6,8) disagree with the result (5) obtained from astrophysical observation. Note however, that eq. (5) assumes the same rate of change over about 10 billion years which doesn't need to be true.

C.   Enhanced relative effects of α variation in atoms

It follows from eq. (1) that the rate at which atomic frequency and α are changing are related by

$$\frac{\delta\omega}{\omega} = \frac{2q}{\omega}\frac{\delta\alpha}{\alpha}, \tag{9}$$

where $K = 2q/\omega$ is an enhancement factor for the relative variation. For the most of "atomic clock transitions" from the ground state to excited metastable states we have $K < 1$ (see Table I) which means no enhancement. However, it is easy to find atomic transitions with

TABLE I: Experimental [16] and theoretical energies and calculated q-coefficients (cm^{-1}) for optical atomic clock transitions from the ground state to an excited metastable state.

Z	Atom	State		E(exp)	E(calc)	q
13	Al II	$3s3p$	$^3P^o_0$	37393	37328	146
		$3s3p$	$^3P^o_1$	37454	37393	211
		$3s3p$	$^3P^o_2$	37578	37524	343
		$3s3p$	$^1P^o_1$	59852	60090	278
20	Ca I	$4s4p$	$^3P^o_0$	15158	15011	125
		$4s4p$	$^3P^o_1$	15210	15066	180
		$4s4p$	$^3P^o_2$	15316	15179	294
		$4s4p$	$^1P^o_1$	23652	24378	250
38	Sr I	$5s5p$	$^3P^o_0$	14318	14169	443
		$5s5p$	$^3P^o_1$	14504	14367	642
		$5s5p$	$^3P^o_2$	14899	14786	1084
		$5s5p$	$^1P^o_1$	21698	22305	924
38	Sr II	$4d$	$^2D_{3/2}$	14556	14550	2828
		$4d$	$^2D_{5/2}$	14836	14880	3172
47	Ag I	$4d^95s^2$	$^2D_{5/2}$	30242	30188	-11300
		$4d^95s^2$	$^2D_{3/2}$	34714	35114	-6500
49	In II	$5s5p$	$^3P^o_0$	42275	42304	3787
		$5s5p$	$^3P^o_1$	43349	43383	4860
		$5s5p$	$^3P^o_2$	45827	45904	7767
		$5s5p$	$^1P^o_1$	63034	62325	6467
56	Ba II	$5d$	$^2D_{3/2}$	4844	5104	6104
		$5d$	$^2D_{5/2}$	5675	6040	6910
70	Yb I	$6s6p$	$^3P^o_0$	17288	16950	2714
		$6s6p$	$^3P^o_1$	17992	17705	3527
		$6s6p$	$^3P^o_2$	19710	19553	5883
		$6s6p$	$^1P^o_1$	25068	26654	4951
70	Yb II	$4f^{13}6s^2$	$^2F^o_{7/2}$	21419	20060	-63752
		$4f^{14}5d$	$^2D_{3/2}$	22961	23942	11438
		$4f^{14}5d$	$^2D_{5/2}$	24333	25503	12582
		$4f^{13}5d6s$	$^3[\frac{3}{2}]^o_{5/2}$	26759	26781	-46863
		$4f^{13}6s6p$	$(\frac{7}{2},0)_{\frac{7}{2}}$	47912	47927	-60432
70	Yb III	$4f^{13}5d$	$(\frac{5}{2},\frac{5}{2})^o_0$	45277	46505	-32800
79	Au I	$5d^96s^2$	$^2D_{5/2}$	9161	9186	-38550
		$5d^96s^2$	$^2D_{3/2}$	21435	22224	-26760
80	Hg I	$6s6p$	$^3P^o_0$	37645	37420	15299
		$6s6p$	$^3P^o_1$	39412	39299	17584
		$6s6p$	$^3P^o_2$	44043	44158	24908
		$6s6p$	$^1P^o_1$	54069	56219	22789
80	Hg II	$5d^96s^2$	$^2D_{5/2}$	35515	35066	-52200
		$5d^96s^2$	$^2D_{3/2}$	50556	50886	-37700
81	Tl II	$6s6p$	$^3P^o_0$	49451	49865	16267
		$6s6p$	$^3P^o_1$	53393	52687	18845
		$6s6p$	$^3P^o_2$	61725	62263	33268
		$6s6p$	$^1P^o_1$	75600	74717	29418
88	Ra II	$6d$	$^2D_{3/2}$	12084	11882	18150
		$6d$	$^2D_{5/2}$	13743	13593	19000

very strong enhancement. One should look for almost degenerate states (small ω) of sufficiently different nature (large Δq), e.g. states of different configurations. A unique example of this kind is dysprosium atom (see Table II). It has a pair of states of opposite parity which are separated by extremely small energy interval ($\sim 10^{-4}$cm^{-1}). Atomic calculations [18, 22] for these states give values of the q coefficients which are large and have opposite signs. This means that the energies of the states move in opposite directions if α is changing thus adding to the enhancement.

An experiment is currently underway at Berkeley to place limits on α variation using this transition [28, 29]. The current limit is $\dot{\alpha}/\alpha = (-2.7\pm2.6)\times10^{-15}$ yr^{-1}. Unfortunately, one of the levels has quite a large linewidth and this limits the accuracy.

Similar pairs of states with strong sensitivity to variation of α can be found in holmium (see Table II) and other Rare-Earth atoms [21].

Another way to find large enhancement is to look for fine structure anomalies [20]. Here both states are of the same configuration and even of the same fine structure multiplet. However strong enhancement may exist due to configuration mixing with other states.

III. ATOMIC MICROWAVE CLOCKS

Hyperfine microwave transitions may be used to search for α-variation [30]. Karshenboim [31] has pointed out that measurements of ratios of hyperfine structure intervals in different atoms are also sensitive to variations in nuclear magnetic moments. However, the magnetic moments are not the fundamental parameters and can not be directly compared with any theory of the variations. Atomic and nuclear calculations are needed for the interpretation of the measurements. We have performed both atomic calculations of α dependence [8, 17, 18, 19, 20, 21, 22] and nuclear calculations of $X_q = m_q/\Lambda_{QCD}$ dependence [32] (see also [33]) for all microwave transitions of current experimental interest including hyperfine transitions in ^{133}Cs, ^{87}Rb, ^{171}Yb$^+$, ^{199}Hg$^+$, ^{111}Cd, ^{129}Xe, ^{139}La, ^{1}H, ^{2}H and ^{3}He.

The dependence of the hyperfine transition frequencies on the variation of α and fundamental mass ratios can be presented in the form [32]

$$\frac{\delta(A/E)}{A/E} = \frac{\delta V}{V}$$

$$V = \alpha^{2+K_{rel}}\left(\frac{m_q}{\Lambda_{QCD}}\right)^{\kappa}\frac{m_e}{m_p}, \qquad (10)$$

where A is the hyperfine structure constant, $E = m_e e^4/\hbar^2$ is atomic unit of energy, m_q is quark mass, Λ_{QCD} is the quantum chromodynamics mass scale, and K_{rel} and κ are sensitivity factors. K_{rel} is the relativistic factor. It is due to the fact that relativistic hfs depends on α stronger that just α^2 as it would be in the nonrelativistic limit. The κ parameter consists of at least two

TABLE II: Experimental and theoretical energies and calculated relativistic energy shifts (q-coefficients, cm^{-1}) for pairs of almost degenerate states of Dy and Ho.

Z Atom	Ground state		Excited state		Energy[cm^{-1}]		q [cm^{-1}]
Configuration	J	Configuration	J	Expt.[16]	Theor.	
66 Dy I	$4f^{10}6s^2$ 8		$4f^{10}5d6s$	10	19797.96	20077	7952
			$4f^95d^26s$	10	19797.96	19693	-25216
67 Ho I	$4f^{11}6s^2$ 15/2		$4f^{10}5d6s^2$	11/2	20493.40	21763	-28200
			$4f^{11}5d6s$	13/2	20493.77	20872	7300
			$4f^{11}6s6p$	13/2	22157.86	22599	3000
			$4f^{11}5d6s$	9/2	22157.88	22631	8000

contributions, $\kappa = \kappa_\mu + \kappa_{hr}$, where κ_μ is due to the dependence of the nuclear magnetic moments on the mass ratio, and κ_{hr} is due to the dependence of the hfs constants on nuclear radius (hadron radius factor). The results of the atomic many-body calculations for K_{rel} [8] and nuclear calculations for κ_μ [32] and κ_{hr} [34] are presented in Table III. One can use these numbers to put limits on the variation of the fundamental constants which follow from the measurements. For example, the frequency ratio Y of the 282-nm $^{199}Hg^+$ optical clock transition to the ground state hyperfine transition in ^{133}Cs was monitored to very high precision for over 6 years at NIST which lead to the following limit on its variation [25]

$$\dot{Y}/Y = (0.37 \pm 0.39) \times 10^{-15} \text{ yr}^{-1}. \qquad (11)$$

Using numbers from Tables I and III one can get the following dependence of this value on the fundamental constants

$$\dot{Y}/Y = -6\dot{\alpha}/\alpha - \dot{\mu}/\mu + 0.02\dot{X}_q/X_q. \qquad (12)$$

Here $X_q = m_q/\Lambda_{QCD}$. For the $\dot{\mu}/\mu$ term we can use the quasar result of Ref. [35] (see section VI B for a detailed discussion)

$$\dot{\mu}/\mu = \dot{X}_e/X_e = (1 \pm 3) \times 10^{-16} \text{ yr}^{-1}, \qquad (13)$$

Where $X_e = m_e/\Lambda_{QCD}$. A combination of this result and the atomic clock result (11) gives one of the best limit on the variation of α:

$$\dot{\alpha}/\alpha = (-8 \pm 8) \times 10^{-17} \text{ yr}^{-1}. \qquad (14)$$

Here we neglected the small ($\sim 2\%$) contribution of X_q. The combined result of Hg^+/Al^+, Yb^+/Cs^+ and Hg^+/Cs^+ gives [24, 25, 27]

$$\dot{\mu}/\mu = \dot{X}_e/X_e = (-0.19 \pm 0.41) \times 10^{-15} \text{ yr}^{-1}. \qquad (15)$$

which does not contradicts to (13).

IV. ENHANCED EFFECT OF VARIATION OF FUNDAMENTAL CONSTANTS IN NUCLEAR SPECTRA (^{229}TH)

There is a very narrow level of 7.6 ± 0.5 eV above the ground state in the ^{229}Th nucleus [36]. The position of this level was determined from the energy differences of many high-energy γ-transitions to the ground and excited states. The subtraction produces the large uncertainty in the position of the 7.6 eV excited state. The width of this level is estimated to be about 10^{-4} Hz [37]. This would explain why it is so hard to find the direct radiation in this very weak transition. However, the search for the direct radiation continues [38].

The ^{229}Th transition is very narrow and can be investigated with laser spectroscopy. This makes ^{229}Th a possible reference for an optical clock of very high accuracy, and opens a new possibility for a laboratory search for the variation of the fundamental constants [39].

As it is shown in Ref. [40] there is an additional very important advantage. According to Ref. [40] the relative effects of variation of α and m_q/Λ_{QCD} are enhanced by 5 orders of magnitude. This estimate has been confirmed by the recent calculation [41] and preliminary results of our new calculations. The accurate results of the calculations will be published soon. A rough estimate for the relative variation of the ^{229}Th transition frequency is

$$\frac{\delta\omega}{\omega} \approx 10^5(0.1\frac{\delta\alpha}{\alpha} + \frac{\delta X_q}{X_q}) \qquad (16)$$

where $X_q = m_q/\Lambda_{QCD}$. Therefore, the Th experiment would have the potential of improving the sensitivity to temporal variation of the fundamental constants by many orders of magnitude. Indeed, we obtain the following energy shift in 7.6 eV ^{229}Th transition:

$$\delta\omega \approx \frac{\delta X_q}{X_q} MeV \qquad (17)$$

This corresponds to the frequency shift $\delta\nu \approx 3 \cdot 10^{20}\delta X_q/X_q$ Hz. The width of this transition is 10^{-4} Hz so one may hope to get the sensitivity to the variation of X_q about 10^{-24} per year. This is 10^{10} times better than the current atomic clock limit on the variation of X_q, $\sim 10^{-14}$ per year.

Note that there are other narrow low-energy levels in nuclei, e.g. 76 eV level in ^{235}U with the 26.6 minutes lifetime (see e.g.[39]). One may expect a similar enhancement there. Unfortunately, this level can not be

TABLE III: Sensitivity of the hyperfine transition frequencies to variation of α (parameter K_{rel}) and to the quark mass/strong interaction scale m_q/Λ_{QCD} (parameter $\kappa = \kappa_\mu + \kappa_{hr}$). These values can be used in equation (10).

Atom	$^{1}_{1}$H	$^{2}_{1}$H	$^{3}_{2}$He	$^{87}_{37}$Rb	$^{111}_{48}$Cd	$^{129}_{54}$Xe	$^{133}_{55}$Cs	$^{139}_{57}$La	$^{171}_{70}$Yb	$^{199}_{80}$Hg
K_{rel}	0	0	0	0.34	0.6	0.8	0.83	0.9	1.5	2.28
κ_μ	-0.100	-0.064	-0.117	-0.016	0.125	0.042	0.009	-0.008	-0.085	-0.088
κ_{hr}	0	0	0	-0.010	-0.018	-0.024	-0.025	-0.028	-0.051	-0.081
κ	-0.100	-0.064	-0.117	-0.026	0.107	0.018	-0.016	-0.036	-0.136	-0.169

reached with usual lasers. In principle, it may be investigated using a free-electron laser or synchrotron radiation. However, the accuracy of the frequency measurements is much lower in this case.

V. ENHANCEMENT OF VARIATION OF FUNDAMENTAL CONSTANTS IN ATOMIC AND MOLECULAR COLLISIONS

Scattering length A, which can be measured in Bose-Einstein condensate and Feshbach molecule experiments, is extremely sensitive to the variation of the electron-to-proton mass ratio $\mu = m_e/m_p$ or $X_e = m_e/\Lambda_{QCD}$ [42].

$$\frac{\delta A}{A} = K\frac{\delta\mu}{\mu} = K\frac{\delta X_e}{X_e}, \qquad (18)$$

where K is the enhancement factor. For example, for Cs-Cs collisions we obtained $K \sim 400$. With the Feshbach resonance, however, one is given the flexibility to adjust position of the resonance using external fields. Near a narrow magnetic or an optical Feshbach resonance the enhancement factor K may be increased by many orders of magnitude.

VI. ENHANCED RELATIVE EFFECT OF VARIATION OF FUNDAMENTAL CONSTANTS IN MOLECULAR SPECTRA

A detailed discussion of the variation of fundamental constants in molecular spectra can be found in recent review [43]. Below we present several examples.

A. Comparison of hydrogen hyperfine and molecular rotational spectra in quasar data

The frequency of the hydrogenic hyperfine line is proportional to $\alpha^2 \mu g_p$ atomic units, molecular rotational frequencies are proportional to μ atomic units. The comparison places limit on the variation of the parameter $F = \alpha^2 g_p$ [44]. Recently similar analysis was repeated by Murphy et al [45] using more accurate data for the same object at $z = 0.247$ and for a more distant object

at $z = 0.6847$, and the following limits were obtained:

$$\frac{\delta F}{F} = (-2.0 \pm 4.4) \times 10^{-6} \qquad (19)$$

$$\frac{\delta F}{F} = (-1.6 \pm 5.4) \times 10^{-6} \qquad (20)$$

The object at $z = 0.6847$ is associated with the gravitational lens toward quasar B0218+357 and corresponds to the backward time ~ 6.5 Gyr.

B. Enhancement of variation of μ in inversion spectrum of ammonia and limit from quasar data

Few years ago van Veldhoven et al suggested to use decelerated molecular beam of ND_3 to search for the variation of μ in laboratory experiments [46]. Ammonia molecule has a pyramidal shape and the inversion frequency depends on the exponentially small tunneling of three hydrogens (or deuteriums) through the potential barrier. Because of that, it is very sensitive to any changes of the parameters of the system, particularly to the reduced mass for this vibrational mode. This fact was used in [35] to place the best limit on the cosmological variation of μ.

The inversion vibrational mode of ammonia is described by a double well potential with first two vibrational levels lying below the barrier. Because of the tunneling, these two levels are split in inversion doublets. The lower doublet corresponds to the wavelength $\lambda \approx 1.25$ cm and is used in ammonia masers. Molecular rotation leads to the centrifugal distortion of the potential curve. Because of that, the inversion splitting depends on the rotational angular momentum J and its projection on the molecular symmetry axis K:

$$\omega_{\text{inv}}(J, K) = \omega_{\text{inv}}^0 - c_1\left[J(J+1) - K^2\right] + c_2 K^2 + \cdots, \qquad (21)$$

where we omitted terms with higher powers of J and K. Numerically, $\omega_{\text{inv}}^0 \approx 23.787$ GHz, $c_1 \approx 151.3$ MHz, and $c_2 \approx 59.7$ MHz.

In addition to the rotational structure (21) the inversion spectrum includes much smaller hyperfine structure. For the main nitrogen isotope ^{14}N, the hyperfine structure is dominated by the electric quadrupole interaction

(~ 1 MHz). Because of the dipole selection rule $\Delta K = 0$ the levels with $J = K$ are metastable. In astrophysics the lines with $J = K$ are also narrower and stronger than others, but the hyperfine structure for spectra with high redshifts is still not resolved. We obtained the following results for NH_3 [35] (in atomic units):

$$\frac{\delta \omega_{\text{inv}}^0}{\omega_{\text{inv}}^0} \approx 4.46 \frac{\delta \mu}{\mu} . \qquad (22)$$

$$\frac{\delta c_{1,2}}{c_{1,2}} = 5.1 \frac{\delta \mu}{\mu} . \qquad (23)$$

For ND_3 the inversion frequency is 15 times smaller and this leads to a higher relative sensitivity of the inversion frequency to μ:

$$\frac{\delta \omega_{\text{inv}}^0}{\omega_{\text{inv}}^0} \approx 5.7 \frac{\delta \mu}{\mu} . \qquad (24)$$

$$\frac{\delta c_{1,2}}{c_{1,2}} = 6.2 \frac{\delta \mu}{\mu} . \qquad (25)$$

We see that the inversion frequency ω_{inv}^0 and the rotational intervals $\omega_{\text{inv}}(J_1, K_1) - \omega_{\text{inv}}(J_2, K_2)$ have different dependencies on the constant μ. In principle, this allows one to study time-variation of μ by comparing different intervals in the inversion spectrum of ammonia. For example, if we compare the rotational interval to the inversion frequency, then Eqs. (22) and (23) give:

$$\frac{\delta \{ [\omega_{\text{inv}}(J_1, K_1) - \omega_{\text{inv}}(J_2, K_2)]/\omega_{\text{inv}}^0 \}}{[\omega_{\text{inv}}(J_1, K_1) - \omega_{\text{inv}}(J_2, K_2)]/\omega_{\text{inv}}^0} = 0.6 \frac{\delta \mu}{\mu} . \qquad (26)$$

The relative effects are substantially larger if we compare the inversion transitions with the transitions between the quadrupole and magnetic hyperfine components. However, in practice this method will not work because of the smallness of the hyperfine structure compared to typical line widths in astrophysics.

We compared the inversion spectrum of NH_3 with rotational spectra of other molecules, where

$$\frac{\delta \omega_{\text{rot}}}{\omega_{\text{rot}}} = \frac{\delta \mu}{\mu} . \qquad (27)$$

High precision data on the redshifts of NH_3 inversion lines exist for already mentioned object B0218+357 at $z \approx 0.6847$ [47]. Comparing them with the redshifts of rotational lines of CO, HCO^+, and HCN molecules from Ref. [48] one can get the following limit:

$$\frac{\delta \mu}{\mu} = \frac{\delta X_e}{X_e} = (-0.6 \pm 1.9) \times 10^{-6}. \qquad (28)$$

Taking into account that the redshift $z \approx 0.68$ for the object B0218+357 corresponds to the backward time about 6.5 Gyr and assuming linear time dependence, this limit translates into the most stringent present limit for the variation rate $\dot{\mu}/\mu$ and X_e [35]:

$$\dot{\mu}/\mu = \dot{X}_e/X_e = (1 \pm 3) \times 10^{-16} \text{ yr}^{-1} . \qquad (29)$$

VII. ENHANCED EFFECTS IN DIATOMIC MOLECULES

In transitions between very close narrow levels of different nature in diatomic molecules the relative effects of the variation may be enhanced by several orders of magnitude. Such levels may occur due to cancellation between either hyperfine and rotational structures [51], or between the fine and vibrational structures of the electronic ground state [49]. The intervals between the levels are conveniently located in microwave frequency range and the level widths are very small, typically $\sim 10^{-2}$ Hz.

A. Molecules with cancellation between hyperfine structure and rotational intervals

Consider diatomic molecules with unpaired electron and ground state $^2\Sigma$. It can be, for example, LaS, LaO, LuS, LuO, YbF, etc. [50]. For a hyperfine interval Δ_{hfs} we have

$$\Delta_{\text{hfs}} \propto \alpha^2 Z F_{\text{rel}}(\alpha Z) \mu g_{\text{nuc}},$$

where F_{rel} is additional relativistic (Casimir) factor. Rotational interval $\Delta_{\text{rot}} \sim \mu$ is roughly independent on α. If we find molecule with $\Delta_{\text{hfs}} \approx \Delta_{\text{rot}}$ the splitting ω between hyperfine and rotational levels will depend on the following combination

$$\omega \sim \left[\alpha^2 F_{\text{rel}}(\alpha Z) g_{\text{nuc}} - \text{const} \right] . \qquad (30)$$

Relative variation is then given by

$$\frac{\delta \omega}{\omega} \approx \frac{\Delta_{\text{hfs}}}{\omega} \left[(2 + K) \frac{\delta \alpha}{\alpha} + \frac{\delta g_{\text{nuc}}}{g_{\text{nuc}}} \right] , \qquad (31)$$

where factor K comes from variation of $F_{\text{rel}}(\alpha Z)$, and for $Z \sim 50$, $K \approx 1$. Using data from [50] one can find that $\omega = (0.002 \pm 0.01)$ cm^{-1} for $^{139}La^{32}S$ [51]. Note that for $\omega = 0.002$ cm^{-1} the relative frequency shift is:

$$\frac{\delta \omega}{\omega} \approx 600 \frac{\delta \alpha}{\alpha} . \qquad (32)$$

B. Molecules with cancellation between fine structure and vibrational intervals

The fine structure interval ω_f rapidly grows with nuclear charge Z:

$$\omega_f \sim Z^2 \alpha^2 , \qquad (33)$$

The vibration energy quantum decreases with the atomic mass:

$$\omega_{\text{vib}} \sim M_r^{-1/2} \mu^{1/2} , \qquad (34)$$

where the reduced mass for the molecular vibration is $M_r m_p$. Therefore, we obtain equation $Z = Z(M_r, v)$

for the lines on the plane Z, M_r, where we can expect approximate cancellation between the fine structure and vibrational intervals:

$$\omega = \omega_f - v\,\omega_{\rm vib} \approx 0\,, \quad v = 1, 2, ... \qquad (35)$$

Using Eqs. (33–35) it is easy to find dependence of the transition frequency on the fundamental constants:

$$\frac{\delta\omega}{\omega} = \frac{1}{\omega}\left(2\omega_f\frac{\delta\alpha}{\alpha} + \frac{v}{2}\omega_{\rm vib}\frac{\delta\mu}{\mu}\right) \approx K\left(2\frac{\delta\alpha}{\alpha} + \frac{1}{2}\frac{\delta\mu}{\mu}\right),$$
$$(36)$$

where the enhancement factor $K = \frac{\omega_f}{\omega}$ determines the relative frequency shift for the given change of fundamental constants. Large values of factor K hint at potentially favorable cases for making experiment, because it is usually preferable to have larger relative shifts. However, there is no strict rule that larger K is always better. In some cases, such as very close levels, this factor may become irrelevant. Thus, it is also important to consider the absolute values of the shifts and compare them to the linewidths of the corresponding transitions.

Because the number of molecules is finite we can not have $\omega = 0$ exactly. However, a large number of molecules have $\omega/\omega_f \ll 1$ and $|K| \gg 1$. Moreover, an additional "fine tuning" may be achieved by selection of isotopes and rotational, Ω-doublet, and hyperfine components. Therefore, we have two large manifolds, the first one is build on the electron fine structure excited state and the second one is build on the vibrational excited state. If these manifolds overlap one may select two or more transitions with different signs of ω. In this case expected sign of the $|\omega|$-variation must be different (since the variation $\delta\omega$ has the same sign) and one can eliminate some systematic effects. Such control of systematic effects was used in [28, 29] for transitions between close levels in two dysprosium isotopes. The sign of energy difference between two levels belonging to different electron configurations was different in ^{163}Dy and ^{162}Dy.

Among the interesting molecules where the ground state is split in two fine structure levels and (35) is approximately fulfilled, there are Cl_2^+ (enhancement $K = 1600$), SiBr ($K = 360$), CuS ($K = 24$) and IrC ($K = 160$). The list of molecules is not complete because of the lack of data in [50]. The molecules Cl_2^+ and SiBr are particularly interesting. For both of them the frequency ω defined by (35) is of the order of 1 cm^{-1} and comparable to the rotational constant B. That means that ω can be reduced further by the proper choice of isotopes, rotational quantum number J and hyperfine components, so we can expect $K \sim 10^3 - 10^5$. New dedicated measurements are needed to determined exact values of the transition frequencies and find the best transitions. However, it is easy to find necessary accuracy of the frequency shift measurements. According to (36) the expected frequency shift is

$$\delta\omega = 2\omega_f\left(\frac{\delta\alpha}{\alpha} + \frac{1}{4}\frac{\delta\mu}{\mu}\right) \qquad (37)$$

Assuming $\delta\alpha/\alpha \sim 10^{-15}$ and $\omega_f \sim 500$ cm^{-1}, we obtain $\delta\omega \sim 10^{-12}$ cm$^{-1} \sim 3 \times 10^{-2}$ Hz (in order to obtain similar sensitivity comparing hyperfine transition frequencies for Cs and Rb one has to measure the shift $\sim 10^{-5}$ Hz). This shift is larger than the natural width $\sim 10^{-2}$ Hz.

C. Molecular ion HfF$^+$

The ion HfF$^+$ and other similar ions are considered by Cornell's group in JILA for the experiment to search for the electric dipole moment (EDM) of the electron. Recent calculation by [52] suggests that the ground state of this ion is $^1\Sigma^+$ and the first excited state $^3\Delta_1$ lies only 1633 cm^{-1} higher. Calculated vibrational frequencies for these two states are 790 and 746 cm^{-1} respectively. For these parameters the vibrational level $v = 3$ of the ground state is only 10 cm^{-1} apart from the $v = 1$ level of the state $^3\Delta_1$. Thus, instead of (35) we now have:

$$\omega = \omega_{\rm el} + \frac{3}{2}\omega_{\rm vib}^{(1)} - \frac{7}{2}\omega_{\rm vib}^{(0)} \approx 0\,, \qquad (38)$$

where superscripts 0 and 1 correspond to the ground and excited electronic states. Electronic transition $\omega_{\rm el}$ is not a fine structure transition and (33) is not applicable. Instead, we can write:

$$\omega_{\rm el} = \omega_{\rm el,0} + qx\,, \quad x = \alpha^2/\alpha_0^2 - 1\,. \qquad (39)$$

Our estimate is [49]

$$\frac{\delta\omega}{\omega} \approx \left(\frac{2q}{\omega}\frac{\delta\alpha}{\alpha} + \frac{\omega_{\rm el}}{2\omega}\frac{\delta\mu}{\mu}\right) \approx \left(2000\frac{\delta\alpha}{\alpha} + 80\frac{\delta\mu}{\mu}\right), \quad (40)$$

$$\delta\omega \approx 20000\ {\rm cm}^{-1}(\delta\alpha/\alpha + 0.04\delta\mu/\mu)\,. \qquad (41)$$

Assuming $\delta\alpha/\alpha \sim 10^{-15}$ we obtain $\delta\omega \sim 0.6$ Hz. The natural width is about 2 Hz.

We also present the result for transition between close levels in Cs$_2$ molecule suggested in [53, 54]. Our estimate is [43]:

$$\delta\omega \approx \left(-240\frac{\delta\alpha}{\alpha} - 1600\frac{\delta\mu}{\mu}\right)cm^{-1}\,, \qquad (42)$$

VIII. CHANGE OF FUNDAMENTAL CONSTANTS NEAR MASSIVE BODIES

Variation of fundamental constants are related to the change of the gravitational potential as [55]

$$\frac{\delta\alpha}{\alpha} = k_\alpha\delta\left(\frac{GM}{rc^2}\right) \qquad (43)$$

$$\frac{\delta(m_q/\Lambda_{QCD})}{(m_q/\Lambda_{QCD})} = k_q\delta\left(\frac{GM}{rc^2}\right) \qquad (44)$$

$$\frac{\delta(m_e/\Lambda_{QCD})}{(m_e/\Lambda_{QCD})} = \frac{\delta(m_e/m_p)}{(m_e/m_p)} = k_e\delta(\frac{GM}{rc^2}) \qquad (45)$$

where in the r.h.s. stands for the half-year variation of Sun's gravitational potential on Earth.

Gravitational potential on Earth is changing due to el-lipticity of its orbit, the corresponding variation of the Sun gravitational potential is $\delta(GM/rc^2) = 3.3 \cdot 10^{-10}$. As an example we consider recent work [25] who obtained the following value for the half-year variation of the frequency ratio of two atomic clocks: (i) optical transitions in mercury ions $^{199}Hg^+$ and (ii) hyperfine splitting in ^{133}Cs (the frequency standard). The limit obtained is

$$\delta ln(\frac{\omega_{Hg}}{\omega_{Cs}}) = (0.7 \pm 1.2) \cdot 10^{-15} \qquad (46)$$

For Cs/Hg frequency ratio of these clocks the dependence on the fundamental constants was evaluated in [32] with the result

$$\delta ln(\frac{\omega_{Hg}}{\omega_{Cs}}) = -6\frac{\delta\alpha}{\alpha} - 0.01\frac{\delta(m_q/\Lambda_{QCD})}{(m_q/\Lambda_{QCD})} - \frac{\delta(m_e/m_p)}{(m_e/m_p)} \qquad (47)$$

Another work [56] compare H and ^{133}Cs hyperfine transitions. The amplitude of the half-year variation found were

$$|\delta ln(\omega_H/\omega_{Cs})| < 7 \cdot 10^{-15} \qquad (48)$$

The sensitivity [32]

$$\delta ln(\frac{\omega_H}{\omega_{Cs}}) = -0.83\frac{\delta\alpha}{\alpha} - 0.11\frac{\delta(m_q/\Lambda_{QCD})}{(m_q/\Lambda_{QCD})} \qquad (49)$$

There is no sensitivity to m_e/m_p because they are both hyperfine transitions.

The results of Cs/Hg frequency ratio measurement [25] can be rewritten in terms of the parameters k_i as in (43,44,45):

$$k_\alpha + 0.17k_e = (3.5 \pm 6.0) \cdot 10^{-7} \qquad (50)$$

The results of Cs/H frequency ratio measurement [56] can be presented as

$$|k_\alpha + 0.13k_q| < 2.5 \cdot 10^{-5} \qquad (51)$$

Finally, the result of recent measurement [57] of Cs/H frequency ratio can be presented as

$$k_\alpha + 0.13k_q = (1 \pm 17) \cdot 10^{-7} \qquad (52)$$

The sensitivity coefficients for other clocks have been discussed above.

Two new results have been obtained recently. From transition between close levels in Dy we obtain [58]

$$k_\alpha = (-8.7 \pm 6.6) \cdot 10^{-6} \qquad (53)$$

From optical Sr/hyperfine Cs comparison we obtained [26]

$$k_\alpha + 0.36k_e = (-2.1 \pm 3.2) \cdot 10^{-6} \qquad (54)$$

Combination of the data gives [26]

$$k_\alpha = (2.5 \pm 3.1) \cdot 10^{-6} \qquad (55)$$

$$k_e = (-1.3 \pm 1.7) \cdot 10^{-5} \qquad (56)$$

$$k_q = (-1.9 \pm 2.7) \cdot 10^{-5} \qquad (57)$$

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